



Promoting effect of MoO₃ on the NO_x reduction by NH₃ over CeO₂/TiO₂ catalyst studied with in situ DRIFTS

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ABSTRACT

A series of MoO₃-doped CeO₂/TiO₂ catalysts prepared by the impregnation method were investigated for the selective catalytic reduction of NO_x by NH₃ (NH₃-SCR). It was found that CeO₂-MoO₃/TiO₂ catalyst is much more active than CeO₂/TiO₂ for NH₃-SCR and the optimum MoO₃ loading is 5%. The mechanistic cause of the promoting effect of MoO₃ on the activity of CeO₂/TiO₂ catalyst for NH₃-SCR was studied using in situ diffuse reflectance infrared transform spectroscopy (DRIFTS). The results revealed that the highly dispersed molybdenum on CeO₂-MoO₃/TiO₂ catalyst not only resulted in more Brønsted acid sites formed on the catalyst surface, but also reduced the thermal stability of the inactive nitrate specie, leaving more active sites available for the adsorption of NH₃, both of which are favorable for the promotion of SCR activity.

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1. Introduction

Nitrogen oxides (NO_x) emitted from mobile and stationary sources are the major air pollutants, as they cause environmental problems such as acid rain, photochemical smog and ozone depletion [1]. Selective catalytic reduction of NO_x with NH₃ (NH₃-SCR) is one effective method for abating NO_x in the flue gas from stationary source and the most widely used catalyst system for this process is V₂O₅-WO₃(MoO₃)/TiO₂ catalyst [2,3]. However, there are still some inevitable problems with this catalyst system including the toxicity of vanadium species, the narrow temperature window of 300–400 °C, the high conversion of SO₂ to SO₃ and the low N₂ selectivity at high temperatures [2,4]. Hence, developing environmentally benign NH₃-SCR catalyst with no vanadium but high catalytic performance is desirable.

Recently, CeO₂ based oxides have attracted increasing attention for their use as NH₃-SCR catalysts due to the high oxygen storage capacity and excellent redox property of CeO₂ [5–9]. Xu et al. [9] reported that Ce/TiO₂ catalyst prepared by impregnation method is active for the NH₃-SCR of NO_x. And the catalyst prepared by sol-gel method showed higher activity than that prepared by impregnation method [10]. The Ce–O–Ti short-range order species with the interaction between Ce and Ti in atomic scale are proposed to be the active sites on the Ce–Ti catalyst by Li et al. [11]. The doping of

tungsten to Ce/TiO₂ leads to the enhanced SCR activity due to the strong interaction between Ce and W [12].

Lietti and co-workers found that the structural and morphological characteristics of MoO₃/TiO₂ and WO₃/TiO₂ are similar, whereas the reactivity was different which may be due to different redox characteristics of the two samples [13,14]. Further studies revealed that the addition of WO₃ and MoO₃ to V₂O₅/TiO₂ are similar, and both oxides acting as “chemical” promoters besides playing a “structural” function as well [15,16]. Considering the similarities of MoO₃ and WO₃ and the lower price of MoO₃ [17], the present work attempts to improve the activity of Ce/TiO₂ catalyst by adding molybdenum oxide to develop a novel non-vanadium NH₃-SCR catalyst with high catalytic activity in a wider temperature window. It was found that the addition of MoO₃ showed a noticeable promoting effect on the activity of Ce/TiO₂ for the NH₃-SCR at relatively low temperatures. On the basis of in situ diffuse reflectance infrared transform spectroscopy (DRIFT) experiments the mechanistic cause of the promoting effect was elucidated.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by impregnation method, and Degussa AEROSIL TiO₂ P25 was used as support. 10 wt.% CeO₂/TiO₂ (Ce₁₀Ti) catalyst was prepared by impregnating TiO₂ with a proper amount of cerium nitrate (Ce(NO₃)₃·6H₂O) solution, then stirred for 4 h, followed by drying at 120 °C and calcinations at 500 °C for

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4 h in air. $\text{MoO}_3/\text{TiO}_2$ catalysts with MoO_3 loading varying from 2–8 wt.% (Mo_xTi) were prepared by the same method as described above using ammonium molybdate $((\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O})$ and oxalic acid $(\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O})$ solution instead. $\text{Ce}_{10}\text{Mo}_x\text{Ti}$ catalyst was prepared by impregnating Mo_xTi powder with an aqueous solution of cerium nitrate, stirred for 4 h, then dried at 120°C and calcined at 500°C for 4 h in air. For comparison, the state-of-the art SCR $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst with 1 wt.% V_2O_5 and 5 wt.% WO_3 was also prepared by the same impregnation method using NH_4VO_3 , $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41}$, $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ as precursors.

2.2. Catalytic activity measurement

The activity measurements were carried out in a fixed-bed quartz reactor using a 0.12 g catalyst of 40–60 meshes. The feed gas mixture contained 500 ppm NO , 500 ppm NH_3 , 5% O_2 and helium as the balance gas. The total flow rate of the feed gas was $300\text{ cm}^3\text{ min}^{-1}$, corresponding to a GHSV of $128,000\text{ h}^{-1}$. The reaction temperature was increased from 200 to 450°C . The composition of the product gas was analyzed by a chemiluminescence NO/NO_2 analyzer (Thermal Scientific, model 42i-HL) and gas chromatograph (Shimadzu GC 2014 equipped with Porapak Q and Molecular sieve 5A columns). The activity data were collected when the catalytic reaction practically reached steady-state condition at each temperature.

2.3. Catalyst characterization

Characterization of the BET surface area of the samples was carried out with a Quantachrome Autosorb AS-1 system. Prior to the surface area measurements, the samples were degassed in vacuum at 400°C for 4 h. Powder X-ray diffraction (XRD) measurements were recorded on a Bruker D8 ADVANCE system with $\text{Cu K}\alpha$ radiation at 45 kV and 200 mA. Temperature-programmed reduction (H_2 -TPR) experiments were conducted on a chemisorption analyzer (Micromeritics, Chemisorb 2720 TPx) under a 10% H_2 gas flow ($50\text{ cm}^3\text{ min}^{-1}$) at a rate of $10^\circ\text{C min}^{-1}$ up to 1000°C .

In situ DRIFTS spectra were recorded using a Thermo Nicolet 6700 spectrometer equipped with a high temperature environmental cell fitted with ZnSe window and an MCT detector cooled with liquid N_2 . The catalyst was loaded in the Harrick IR cell and heated to 400°C under helium at a total flow rate of $100\text{ cm}^3\text{ min}^{-1}$ for 60 min to remove adsorbed impurities. A background spectrum was collected under a flowing helium atmosphere and was subtracted from the sample spectra. The DRIFTS spectra were recorded by accumulating 100 scans with a resolution of 4 cm^{-1} .

3. Results and discussion

3.1. NH_3 -SCR activity

NH_3 -SCR activities of CeTi , MoTi and CeMoTi catalysts were evaluated as a function of temperature and the results are presented in Fig. 1. It is evident that the addition of 2% Mo to Ce_{10}Ti showed a remarkable promoting effect below 325°C . With the increasing of MoO_3 loadings from 2% to 5%, NO_x conversion was further increased. Further increasing the Mo loading to 8% leads to a decrease of the activity, but it is still higher than that of Ce_{10}Ti catalyst below 275°C . Therefore, the optimum loading of MoO_3 is 5%. For $\text{Ce}_{10}\text{Mo}_5\text{Ti}$ catalyst, nearly 90% of NO_x conversion was obtained in a wide temperature range ($275\text{--}400^\circ\text{C}$) under a high GHSV of $128,000\text{ h}^{-1}$. And the NO_x conversion starts to decrease when the temperature is higher than 400°C . Compared with Ce_{10}Ti and Mo_5Ti catalysts, $\text{Ce}_{10}\text{Mo}_5\text{Ti}$ exhibited much higher activity below 325°C , indicating that the coexistence of Ce and a proper amount of Mo is very important for the SCR activity.

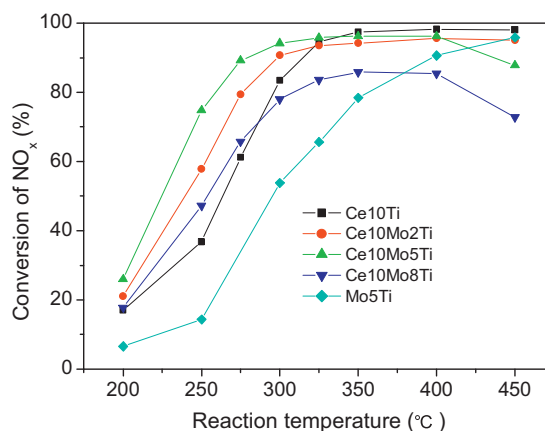


Fig. 1. Activities of Ce_{10}Ti , Mo_5Ti and $\text{Ce}_{10}\text{Mo}_x\text{Ti}$ with various Mo loading for the NO_x reduction with NH_3 . Reaction conditions: $[\text{NO}] = [\text{NH}_3] = 500\text{ ppm}$, $[\text{O}_2] = 5\%$, GHSV = $128,000\text{ h}^{-1}$.

Fig. 2 showed the comparison of the SCR activities of $\text{Ce}_{10}\text{Mo}_5\text{Ti}$ and $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts. It can be seen that $\text{Ce}_{10}\text{Mo}_5\text{Ti}$ is more active than the conventional $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ below 325°C . Therefore, the environmentally benign $\text{Ce}_{10}\text{Mo}_5\text{Ti}$ catalyst is promising for the control of NO_x emitted from stationary source.

3.2. BET surface area, XRD and H_2 -TPR

As shown in Table S1, the surface area of Ce_{10}Ti decreased after doping MoO_3 and $\text{Ce}_{10}\text{Mo}_8\text{Ti}$ is of the lowest surface area. This is in accordance with the previous report that the BET surface area of the catalyst decreases as the molybdenum loading increases [14,18]. Although the BET surface area of $\text{Ce}_{10}\text{Mo}_5\text{Ti}$ was lower than that of Ce_{10}Ti catalyst, it exhibited higher NH_3 -SCR activity, indicating that some synergistic effect existed between Ce and Mo species and the BET surface area does not play a key role in the SCR reaction.

Fig. 3 showed the XRD patterns of TiO_2 , Ce_{10}Ti , Mo_5Ti and $\text{Ce}_{10}\text{Mo}_x\text{Ti}$ with different Mo loading. For all the catalysts, the anatase phase (PDF-ICDD21-1272) was the main phase, and only a little rutile phase (PDF-ICDD21-1276) appeared. It is well worthy to note that the peak ascribed to crystalline MoO_3 phase was absent for $\text{Ce}_{10}\text{Mo}_x\text{Ti}$ and Mo_5Ti catalysts, indicating that the molybdenum oxide was highly dispersed on the surface of TiO_2 . A weak peak of cubic CeO_2 crystallites was observed over Ce_{10}Ti catalyst [11]. The peak ascribed to CeO_2 becomes more noticeable after the addition of MoO_3 to Ce_{10}Ti catalyst, indicating that the introduction of Mo

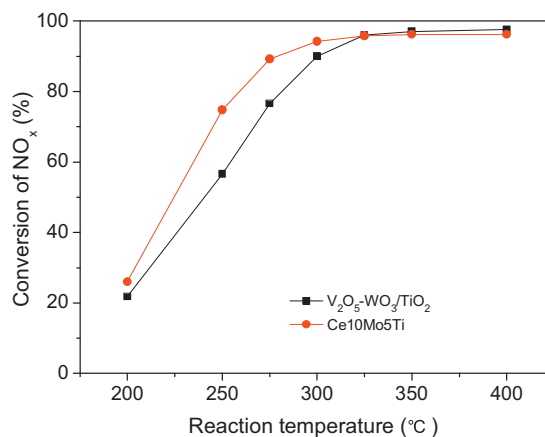


Fig. 2. Comparison of NH_3 -SCR activities of $\text{Ce}_{10}\text{Mo}_5\text{Ti}$ and $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts. Reaction conditions: $[\text{NO}] = [\text{NH}_3] = 500\text{ ppm}$, $[\text{O}_2] = 5\%$, GHSV = $128,000\text{ h}^{-1}$.

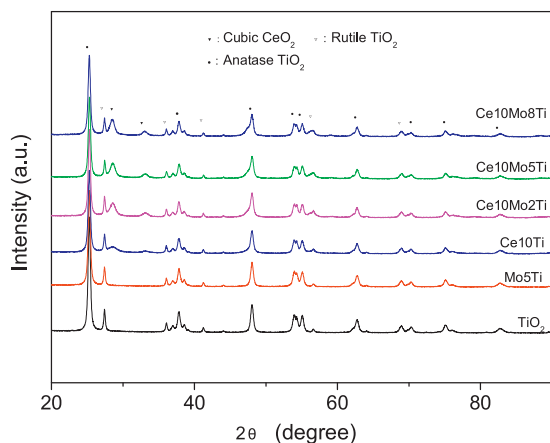


Fig. 3. XRD patterns of TiO_2 , Ce_{10}Ti , Mo_5Ti and $\text{Ce}_{10}\text{Mo}_x\text{Ti}$ with different Mo loading.

could induce the crystallite of CeO_2 . The presence of crystallite CeO_2 could enhance the combustion of NH_3 with oxygen at high temperatures, thus relatively less NH_3 remained for the NH_3 -SCR, resulting the decrease of NO_x conversion (see Fig. 1).

Fig. 4 presents the H_2 -TPR profiles on Ce_{10}Ti , Mo_5Ti and $\text{Ce}_{10}\text{Mo}_5\text{Ti}$ catalysts. For Ce_{10}Ti catalyst, three reduction peaks centering at 450, 590 and 940 °C appeared. The two reduction peaks at 450 and 590 °C can be attributed to the reduction of Ce^{4+} to Ce^{3+} [19,20], and the peak at 940 °C might be due to the reduction of bulk CeO_2 [20]. Mo_5Ti also exhibited three reduction peaks at around 400, 500 and 735 °C. The first two peaks could be assigned to the reduction of the octahedral well dispersed Mo species and the high temperature reduction peak (735 °C) could be due to the reduction of tetrahedral Mo species [21], which is in strong interaction with TiO_2 support. Interestingly, $\text{Ce}_{10}\text{Mo}_5\text{Ti}$ catalyst possesses two main reduction peaks centering at 460 and 880 °C. The former one could be assigned to the coreduction of surface Ce^{4+} and octahedral well dispersed Mo species, and the latter one is due to the coreduction of bulk CeO_2 and tetrahedral Mo species. This fact suggests that the synergetic interaction between Ce and Mo exists in $\text{Ce}_{10}\text{Mo}_5\text{Ti}$ catalyst, which could contribute to the enhanced SCR activity below 325 °C.

3.3. In situ DRIFTS studies

3.3.1. Adsorption of NH_3

Fig. 5(a) showed the DRIFT spectra of NH_3 adsorption over Ce_{10}Ti catalyst at different temperatures. The bands at 1592 and 1157 cm^{-1} with shoulder at 1221 cm^{-1} can be assigned to

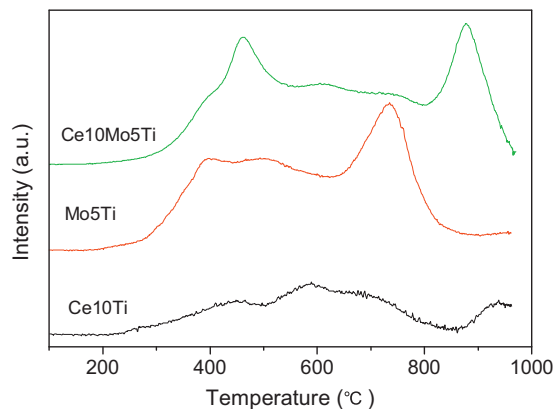


Fig. 4. H_2 -TPR profiles on Ce_{10}Ti , Mo_5Ti and $\text{Ce}_{10}\text{Mo}_5\text{Ti}$ catalysts.

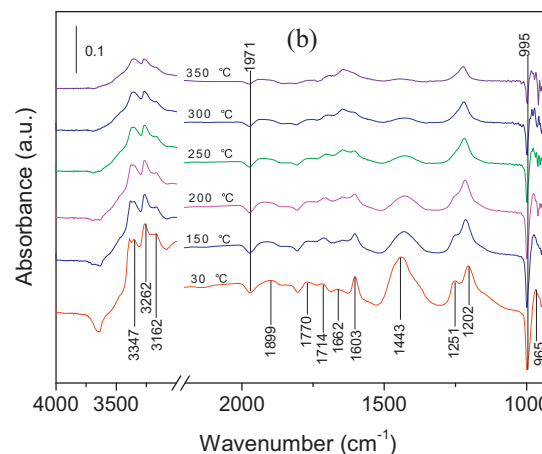
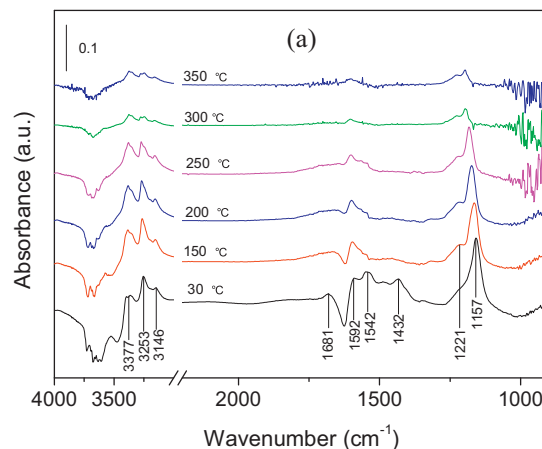


Fig. 5. DRIFT spectra of Ce_{10}Ti (a) and $\text{Ce}_{10}\text{Mo}_5\text{Ti}$ (b) treated in flowing 500 ppm NH_3 at room temperature for 60 min and then purged by He at 30, 150, 200, 250, 300, and 350 °C.

asymmetric and symmetric bending vibrations of the coordinated NH_3 linked to Lewis acid sites [15,22], and that at 3377, 3253 and 3146 cm^{-1} can be ascribed to the N-H stretching vibration modes of the coordinated NH_3 [23]. The band at around 1542 cm^{-1} is ascribed to amid ($-\text{NH}_2$) species [15,23]. The weak bands assigned to asymmetric and symmetric bending vibrations of NH_4^+ species on Brønsted acid sites (1432 and 1681 cm^{-1}) [24,25] were also observed. With increasing temperature, the intensity of the bands assigned to Brønsted acid sites decreased noticeably than that of the bands due to Lewis acid sites. This indicates that ammonia bonded to Lewis acid sites were more stable than that on Brønsted acid sites [26].

As shown in Fig. 5(b), the DRIFT spectra of NH_3 adsorption over $\text{Ce}_{10}\text{Mo}_5\text{Ti}$ catalyst were much different from that of Ce_{10}Ti catalyst. Besides the observed coordinated NH_3 linked to Lewis acid sites (1202, 1251, 1603, 3162, 3262 and 3347 cm^{-1}), a new band appeared at 965 cm^{-1} , which could be assigned to weakly adsorbed or gas phase NH_3 [27,28]. It is evident that the intensity of the band assigned to Brønsted acid sites (1443 cm^{-1}) is much higher than that over Ce_{10}Ti catalyst. Several bands appeared in the range of 1850–1640 cm^{-1} could also be assigned to NH_4^+ species on Brønsted acid sites. Whereas only one band appear in this range over Ce_{10}Ti catalyst as described above. These results suggest that the introduction of Mo tremendously increased both the quantity and the intensity of Brønsted acid sites on the catalyst. Previous research showed that Brønsted acid site is beneficial for the adsorption of NH_3 thus improving the low-temperature activity [26,29]. All the bands decreased with increasing temperature.

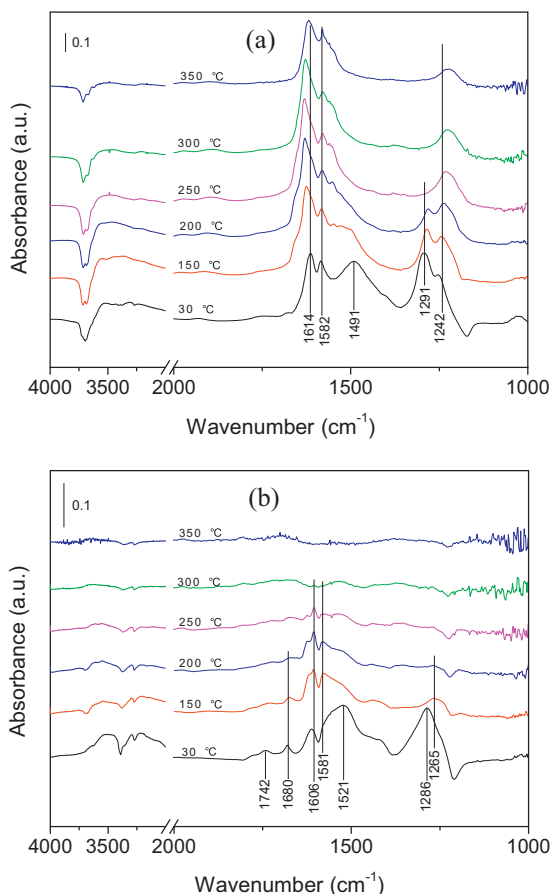


Fig. 6. DRIFT spectra of Ce_{10}Ti (a) and $\text{Ce}_{10}\text{Mo}_5\text{Ti}$ (b) treated in flowing 500 ppm $\text{NO} + 5\% \text{O}_2$ at room temperature for 60 min and then purged by He at 30, 150, 200, 250, 300, and 350 °C.

It should be noted that two negative bands around 1000 and 1971 cm^{-1} formed over $\text{Ce}_{10}\text{Mo}_5\text{Ti}$ catalyst. The similar bands were also observed over the Mo_5Ti catalyst (see Fig. S1). Therefore, the negative band is supposed to be due to the molybdenum of the catalyst. Previous study revealed that these two negative bands correspond to the first overtone and the fundamental stretching mode of a single short $\text{Mo}=\text{O}$ bond of a surface isolated molybdenyl species, respectively [30–32]. This means that molybdenyl species are unsaturated on the catalyst surface and are perturbed by ammonia adsorption, leading to lower $\text{Mo}=\text{O}$ bond order. Therefore, Molybdenyl species act as adsorption sites for ammonia adsorption, which is in agreement with previous report [23].

3.3.2. Co-adsorption of NO and O_2

The DRIFT spectra of $\text{NO} + \text{O}_2$ on Ce_{10}Ti catalyst at different temperatures were illustrated in Fig. 6(a). Several distinct bands appeared at 1242, 1291, 1491, 1582 and 1614 cm^{-1} , which were respectively assigned to the asymmetric frequency of gaseous NO_2 molecules (1614 cm^{-1}) [26], bidentate nitrate (1582 cm^{-1}) [33], monodentate nitrate (1291 and 1491 cm^{-1}) [34] and bridged nitrate (1242 cm^{-1}) [35]. It can be seen that the monodentate nitrate is instable and their intensity decreased with increasing temperature.

Fig. 6(b) showed the DRIFT spectra of NO_x adsorption over $\text{Ce}_{10}\text{Mo}_5\text{Ti}$ catalyst, which was much different from that of Ce_{10}Ti . With the Mo addition, all the bands showed less thermal stability. The bands at 1291 and 1491 cm^{-1} ascribed to the instable monodentate nitrate shifted to 1286 and 1521 cm^{-1} and appeared only at room temperature. The peaks attributed to

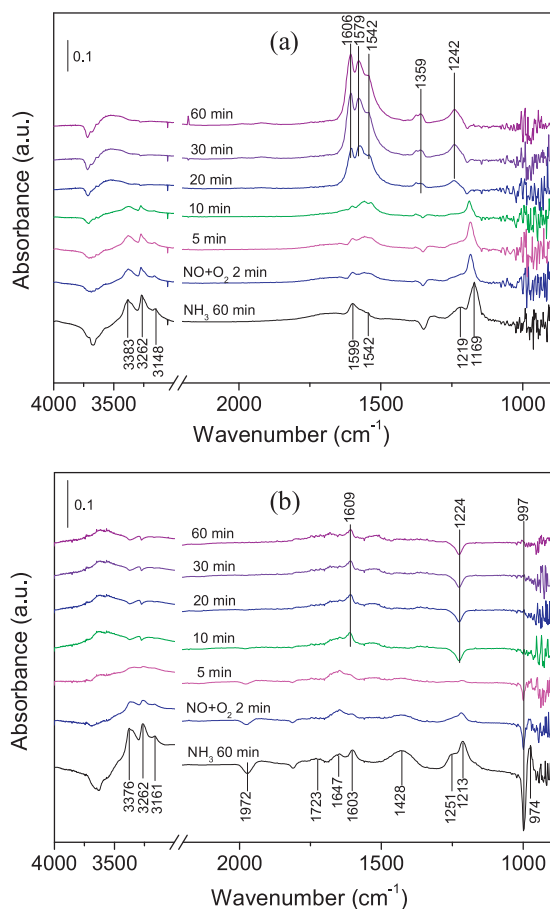


Fig. 7. Dynamic changes of the in situ DRIFT spectra over Ce_{10}Ti (a) and $\text{Ce}_{10}\text{Mo}_5\text{Ti}$ (b) catalysts as a function of time in a flow of $\text{NO} + \text{O}_2$ after the catalysts was pre-exposed to a flow of NH_3 for the 60 min followed by helium purging for 30 min at 250 °C.

bidentate nitrate (1581 cm^{-1}) and gaseous NO_2 molecules (1606 cm^{-1}) vanished at 250 and 300 °C, respectively. The bridged nitrate species (1242 cm^{-1}) was not observed. The two new bands at 1680 and 1742 cm^{-1} could be assigned to N_2O_4 [36] and $\text{trans}(\text{NO})_2$ [37], respectively. All these results suggest that the addition of Mo significantly reduced the thermal stability of the absorbed nitrate species and changed their forms as well.

3.3.3. Reaction between nitrogen oxides and ammonia adspecies

Fig. 7 showed the DRIFT spectra of Ce_{10}Ti and $\text{Ce}_{10}\text{Mo}_5\text{Ti}$ catalysts in a flow of $\text{NO} + \text{O}_2$ after the catalysts was pre-exposed to a flow of NH_3 for the 60 min followed by helium purging for 30 min at 250 °C. As shown in Fig. 7 (a), the coordinated NH_3 on Lewis acid sites (1169 , 1219 and 1599 cm^{-1}) and $-\text{NH}_2$ species (1542 cm^{-1}) formed on Ce_{10}Ti catalyst with feeding NH_3 . Switching the gas to $\text{NO} + \text{O}_2$, the intensities of all bands assigned to ammonia species decreased and the bands vanished in 10 min. Meanwhile some new bands attributed to NO_x species (1242 , 1542 , 1606 , 1579 cm^{-1}) appeared. The band at 1359 cm^{-1} could be assigned to the intermediate species from the combination of surface adsorbed NH_3 and NO_x species [26].

Compared with Ce_{10}Ti , all the bands due to ammonia adspecies and the two negative bands at 997 and 1972 cm^{-1} vanished in 2 min after $\text{Ce}_{10}\text{Mo}_5\text{Ti}$ catalyst was purged by $\text{NO} + \text{O}_2$, and subsequently the absorbed NO_2 (1609 cm^{-1}) and bridged nitrate (1224 cm^{-1}) were observed (see Fig. 7(b)). The band assigned to the combination of surface adsorbed NH_3 and NO_x species (1359 cm^{-1}) is absent. Another interesting phenomenon is that only one band related

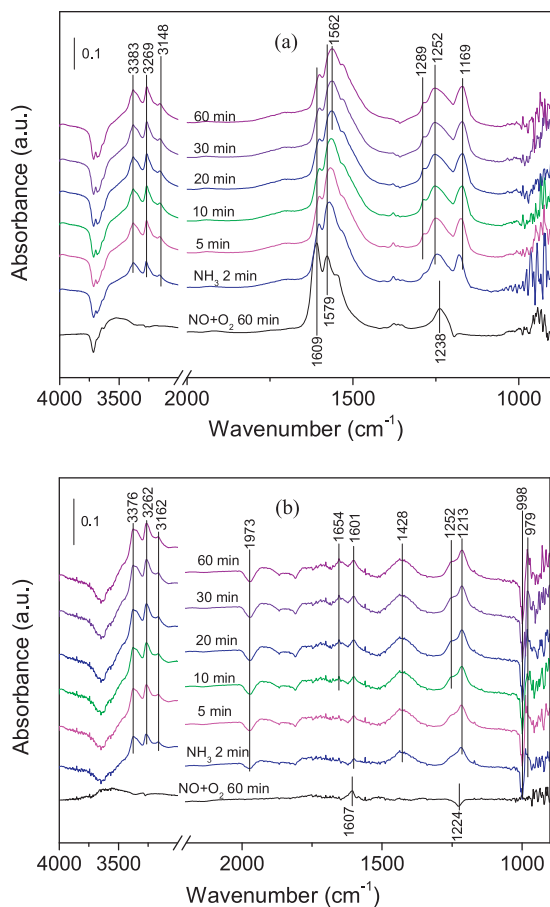


Fig. 8. Dynamic changes of the in situ DRIFT spectra over Ce_{10}Ti (a) and $\text{Ce}_{10}\text{Mo}_5\text{Ti}$ (b) catalysts as a function of time in a flow of NH_3 after the catalysts were pre-exposed to a flow of $\text{NO} + \text{O}_2$ for the 60 min followed by helium purging for 30 min at 250°C .

to NO_2 appeared, indicating that the adsorption of nitrate species was inhibited. The possible reason is that the addition of MoO_3 to Ce_{10}Ti catalyst leads to more acid sites formed with reduced the alkali sites where nitrate species adsorbed. From the comparison between Fig. 7(a) and (b) it can be seen that the adsorbed ammonia species on $\text{Ce}_{10}\text{Mo}_5\text{Ti}$ are more reactive than those on Ce_{10}Ti to react with NO_x , leading to the enhanced SCR activity of NO_x .

3.3.4. Reaction between ammonia and adsorbed nitrogen oxides species

Fig. 8 showed the DRIFT spectra of Ce_{10}Ti and $\text{Ce}_{10}\text{Mo}_5\text{Ti}$ catalysts in a flow of NH_3 after the catalysts were pre-exposed to a flow of $\text{NO} + \text{O}_2$ for the 60 min followed by N_2 purging for 30 min at 250°C . As illustrated in Fig. 8 (a), switching the gas to NH_3 leads to an immediate decrease in the intensity of NO_2 peak (1609 cm^{-1}). And the peak ascribed to the coordinated NH_3 (1600 and 1169 cm^{-1}) with the N–H stretching vibration modes of it (3148 , 3269 , 3383 cm^{-1}) appeared. The peak at 1579 cm^{-1} shifted to the lower frequency gradually with feeding NH_3 , which could be the overlap of the NH_2 species and the bidentate nitrate species. The band at 1238 cm^{-1} ascribed to the bridging nitrate species transformed to two bands at 1289 and 1252 cm^{-1} , both of which might be due to the nitrate species formed by the oxidation of ammonia or the interaction between ammonia and adsorbed NO_x species [26].

As shown in Fig. 8(b), over $\text{Ce}_{10}\text{Mo}_5\text{Ti}$ catalyst the peak assigned to NO_2 (1606 cm^{-1}) diminished in 2 min after NH_3 was introduced into the system. Simultaneously, the peaks ascribed to coordinated NH_3 on Lewis acid sites (3376 , 3262 , 3162 , 1601 , 1213 cm^{-1} with a shoulder at 1252 cm^{-1}) and NH_4^+ species on Brønsted acid sites

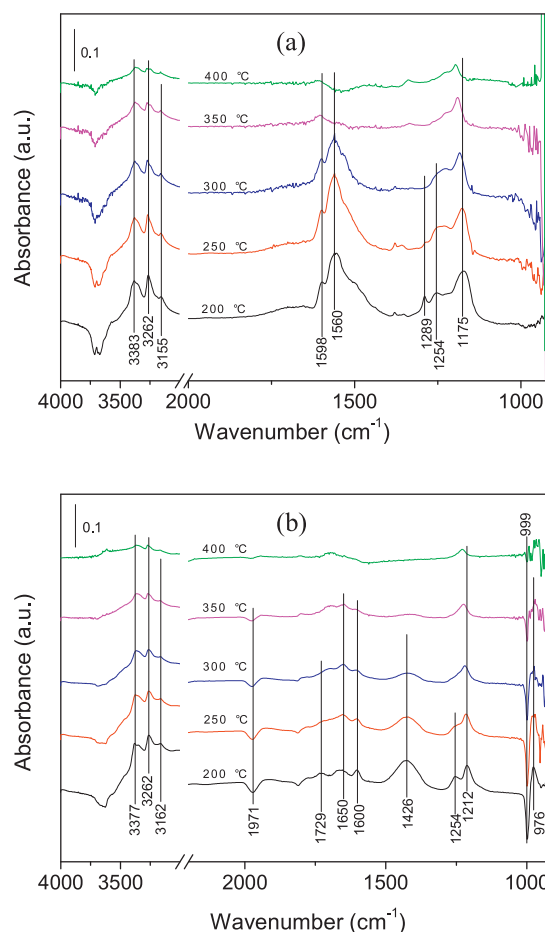


Fig. 9. DRIFT spectra of Ce_{10}Ti (a) and $\text{Ce}_{10}\text{Mo}_5\text{Ti}$ (b) in a flowing of 500 ppm NH_3 + 500 ppm NO + 5% O_2 at 200 , 250 , 300 , 350 and 400°C .

(1428 and 1654 cm^{-1}) appeared. The band at 965 cm^{-1} assigned to weakly adsorbed or gas phase NH_3 were also observed. All the results indicated that the reaction between adsorbed NO_2 and NH_3 easily occurred, especially over $\text{Ce}_{10}\text{Mo}_5\text{Ti}$ catalysts, but the adsorbed nitrate species was unlikely to react with ammonia. With Mo addition, the adsorption of nitrate species was significantly limited as shown in Fig. 6(b), leading to more active sites available for the adsorption and activation of NH_3 thus a higher activity.

3.3.5. DRIFT spectra in a flow of $\text{NO} + \text{NH}_3 + \text{O}_2$

Fig. 9 showed the in situ DRIFT spectra of Ce_{10}Ti and $\text{Ce}_{10}\text{Mo}_5\text{Ti}$ catalysts at various temperatures during the reaction of 500 ppm NH_3 , 500 ppm NO and 5% O_2 under the steady-state condition. On Ce_{10}Ti (see Fig. 9(a)) catalyst, bands due to various nitrate species were observed at 1254 , 1289 , and 1560 cm^{-1} . The intensities of these bands are still high until 300°C , suggesting that the nitrate species were not reactive. Above 300°C these peaks disappeared quickly. The peaks ascribed to the coordinated NH_3 on Lewis acid sites (3383 , 3262 , 3155 , 1598 and 1175 cm^{-1}) were also observed. But the bands due to NH_4^+ species on Brønsted acid sites are absent.

As presented in Fig. 9(b), the DRIFT spectra over $\text{Ce}_{10}\text{Mo}_5\text{Ti}$ are quite different from that over Ce_{10}Ti catalyst. No band due to nitrate species was detected in the whole region, which might be caused by the competitive adsorption and followed reactions among NH_3 , NO and O_2 . Different from the adsorption on Ce_{10}Ti catalyst, both the coordinated NH_3 on Lewis acid sites (1254 and 1212 cm^{-1}) and NH_4^+ species on Brønsted acid sites (1426 , 1650 and 1729 cm^{-1}) were observed on $\text{Ce}_{10}\text{Mo}_5\text{Ti}$.

For the NH_3 -SCR process, the Langmuir–Hinshelwood (L-H) and Eley–Rideal (E-R) mechanisms are two of the most accepted mechanism [7,26,38]. From the dynamic changes of the in situ DRIFT spectra of nitrate species after feeding NH_3 over Ce_{10}Ti and $\text{Ce}_{10}\text{Mo}_5\text{Ti}$ catalyst (see Fig. 8), it can be seen that the formed nitrate species unlikely participated in the SCR reaction. These generated thermally stable nitrates (NO_3^-) covered the surface active sites to prohibit the adsorption of NH_3 , thus showing harmful effects for NH_3 -SCR reaction. The similar harmful effect of nitrates was also proposed for cryptomelane-type manganese oxides (OMS-2) catalyst by Sun et al. [39]. For various catalytic systems, different hypotheses have been proposed for the mechanism. However, the adsorption and activation of NH_3 are recognized to be a key step [7,40]. For the Ce_{10}Ti catalyst, Lewis acid sites were considered to be the main active sites as shown in Fig. 5(a). NO_2 was also formed as observed in the stable and transient experiment (see Fig. 6(a) and Fig. 8(a)). Below 300°C , the coordinated NH_3 reacted with adsorbed NO_2 to form N_2 (L-H mechanism). When the reaction temperature is higher than 300°C , coordinated NH_3 species reacted with gaseous NO to form nitrite and nitrate which then decomposed to N_2 (E-R mechanism).

Chen et al. [12] found that the addition of tungsten oxide to $\text{CeO}_2/\text{TiO}_2$ catalyst can promote the NO oxidation to NO_2 , which is beneficial for the SCR reaction. In the present study, the addition of Mo to $\text{CeO}_2/\text{TiO}_2$ catalyst does not contribute to the formation of NO_2 , as indicated by the DRIFT spectra in Fig. 6. In comparison with tungsten, the presence of Mo on $\text{Ce}_{10}\text{Mo}_5\text{Ti}$ catalyst is unsaturated. The unsaturated Mo resulted in more Brønsted acid sites formed on the catalyst surface (see Fig. 5(b)), which was favorable for the adsorption of NH_3 thus improving the low-temperature activity [26,29,41]. Anstrom et al. [42] reported a mechanism by using density functional theory calculations that NO reacted with adsorbed NH_4^+ to NH_3HNO , which reacted further to yield the NH_2NO . Then the NH_2NO decomposed to form N_2 and H_2O . Both the coordinated NH_3 on Lewis acid sites and the NH_4^+ on Brønsted acid sites were considered to be involved in the SCR reaction over $\text{Ce}_{10}\text{Mo}_5\text{Ti}$ catalyst. On one hand, they can react with the adsorbed NO_2 (L-H mechanism), on the other hand, they will react with the gas phase NO (E-R mechanism) followed the reaction route as proposed by Anstrom et al. [42].

In summary, the addition of Mo to Ce_{10}Ti catalyst prevents the formation of stable nitrate, leaving more active sites available for the adsorption of NH_3 . Moreover, more Brønsted acid sites formed on the catalyst surface due to the presence of Mo, which appeared to be important for the high SCR activity. Mo also could contribute to the activation of adsorbed NH_3 and NH_4^+ , making them react with NO_x more easily.

4. Conclusions

$\text{CeO}_2\text{-MoO}_3/\text{TiO}_2$ catalyst is much more active than $\text{CeO}_2/\text{TiO}_2$ for the NH_3 -SCR at relatively low temperatures and the optimum MoO_3 loading is 5%. Based on the in situ DRIFTS studies, it is proposed that the role of MoO_3 is to prevent the formation of stable nitrate species but to promote the formation of Brønsted acid sites, both of which contribute to the adsorption and activation of NH_3 on the catalyst surface, resulting in the higher activity of $\text{CeO}_2\text{-MoO}_3/\text{TiO}_2$ in comparison to $\text{CeO}_2/\text{TiO}_2$.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2013.06.036>.

References

- [1] Z. Liu, J. Hao, L. Fu, T. Zhu, *Appl. Catal. B* 44 (2003) 355–370.
- [2] G. Busca, L. Lietti, G. Ramis, F. Berti, *Appl. Catal. B* 18 (1998) 1–36.
- [3] Z.M. Liu, S.I. Woo, *Catal. Rev. – Sci. Eng.* 48 (2006) 43–89.
- [4] S. Brandenberger, O. Kröcher, A. Tissler, R. Althoff, *Catal. Rev. – Sci. Eng.* 50 (2008) 492–531.
- [5] K. Krishna, G.B.F. Seijger, C.M. Bleek, H.P.A. Calis, *Chem. Commun.* 18 (2002) 2030–2031.
- [6] G. Qi, R.T. Yang, *Chem. Commun.* 7 (2003) 848–849.
- [7] G. Qi, R.T. Yang, R. Chang, *Appl. Catal. B* 51 (2004) 93–106.
- [8] Y. Li, H. Cheng, D.Y. Li, Y.S. Qin, Y.M. Xie, S.D. Wang, *Chem. Commun.* 12 (2008) 1470–1472.
- [9] W.Q. Xu, Y.B. Yu, C.B. Zhang, H. He, *Catal. Commun.* 9 (2008) 1453–1457.
- [10] X. Gao, Y. Jiang, Y.C. Fu, Y. Zhong, Z.Y. Luo, K.F. Cen, *Catal. Commun.* 11 (2010) 465–469.
- [11] P. Li, Y. Xin, Q. Li, Z.P. Wang, Z.L. Zhang, L.R. Zheng, *Environ. Sci. Technol.* 46 (2012) 9600–9605.
- [12] L. Chen, J.H. Li, M.F. Ge, R.H. Zhu, *Catal. Today* 153 (2010) 77–83.
- [13] L. Lietti, P. Forzatti, F. Berti, *Catal. Lett.* 41 (1996) 35–39.
- [14] I. Nova, L. Lietti, L. Casagrande, L. Dall'Acqua, E. Giamello, P. Forzatti, *Appl. Catal. B* 17 (1998) 245–258.
- [15] L. Lietti, I. Nova, G. Ramis, L. Dall'Acqua, G. Busca, E. Giamello, P. Forzatti, F. Bregani, *J. Catal.* 187 (1999) 419–435.
- [16] L. Casagrande, L. Lietti, I. Nova, P. Forzatti, A. Baiker, *Appl. Catal. B* 22 (1999) 63–77.
- [17] H.L. Koh, H.K. Park, *J. Ind. Eng. Chem.* 19 (2013) 73–79.
- [18] H. Matralis, S. Theret, Ph Bastians, M. Ruwet, P. Grange, *Appl. Catal. B* 5 (1995) 271–281.
- [19] H. Chen, A. Sayari, A. Adnot, F. Larachi, *Appl. Catal. B* 32 (2001) 195–204.
- [20] A. Trovarelli, G. Dolcetti, C. de Leitenburg, J. Kašpar, P. Finetti, A. Santoni, *J. Chem. Soc., Faraday Trans.* 88 (1992) 1311–1319.
- [21] L.C. Caero, A.R. Romero, J. Ramirez, *Catal. Today* 78 (2003) 513–518.
- [22] M.A. Larrubia, G. Ramis, G. Busca, *Appl. Catal. B* 27 (2000) L145–L151.
- [23] L. Dall'Acqua, I. Nova, L. Lietti, G. Ramis, G. Busca, E. Giamello, *Phys. Chem. Chem. Phys.* 2 (2000) 4991–4998.
- [24] P.G. Smirniotis, D.A. Peña, B.S. Uphade, *Angew. Chem. Int. Ed.* 40 (2001) 2479–2482.
- [25] S.D. Lin, A.C. Gluhoi, B.E. Nieuwenhuys, *Catal. Today* 90 (2004) 3–14.
- [26] L. Chen, J.H. Li, M.F. Ge, *Environ. Sci. Technol.* 44 (2010) 9590–9596.
- [27] Y. Peng, Z.M. Liu, W. Han, J.H. Li, *Catal. Commun.* 19 (2012) 127–131.
- [28] Z.B. Wu, B.Q. Jiang, Y. Liu, H.Q. Wang, R.B. Jin, *Environ. Sci. Technol.* 41 (2007) 5812–5817.
- [29] G. Zhou, B. Zhong, W. Wang, X. Guan, B. Huang, D. Ye, H. Wu, *Catal. Today* 175 (2011) 157–163.
- [30] M. Del Arco, C. Martín, V. Rives, V. Sánchez-Escribano, G. Ramis, G. Busca, V. Lorenzelli, P. Malet, *J. Chem. Soc., Faraday Trans.* 89 (1993) 1071.
- [31] G. Busca, J.C. Lavalley, *Spectrochim. Acta, Part A* 42 (1986) 443–445.
- [32] E. Payen, S. Kasztelan, J. Grimblot, J.P. Bonnelle, *J. Raman Spectrosc.* 17 (1986) 233–241.
- [33] A. Trovarelli, *Catal. Rev. – Sci. Eng.* 38 (1996) 439–520.
- [34] G.M. Underwood, T.M. Miller, V.H. Grassian, *J. Phys. Chem. A* 103 (1999) 6184–6190.
- [35] Y. Chi, S.S.C. Chuang, *Catal. Today* 62 (2000) 303–318.
- [36] J. Vályi, W.K. Hall, *J. Phys. Chem.* 97 (1993) 1204–1212.
- [37] A. Martínez-Arias, J. Soria, J.C. Conesa, X.L. Seoane, A. Arcoya, R. Cataluña, *J. Chem. Soc., Faraday Trans.* 91 (1995) 1679–1687.
- [38] W.S. Kijlstra, D.S. Brands, H.I. Smit, E.K. Poels, A. Bliek, *J. Catal.* 171 (1997) 219–230.
- [39] L. Sun, Q. Cao, B. Hu, J. Li, J. Hao, G. Jing, X. Tang, *Appl. Catal. A* 393 (2011) 323–330.
- [40] G. Qi, R.T. Yang, *J. Catal.* 217 (2003) 434–441.
- [41] Y. Shu, H. Sun, X. Quan, S. Chen, *J. Phys. Chem. C* 116 (2012) 25319–25327.
- [42] M. Anstrom, N.-Y. Topsøe, J.A. Dumesic, *J. Catal.* 213 (2003) 115–125.